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71 Applicant: **TOYOTA JIDOSHA KABUSHIKI KAISHA**
1, Toyota-cho
Toyota-shi
Aichi-ken 471(JP)

72 Inventor: Goto, Masato
c/o Toyota Jidosha Kabushiki Kaisha,
1, Toyota-cho
Toyota-shi, Aichi-ken(JP)
Inventor: Iguchi, Satoshi
c/o Toyota Jidosha Kabushiki Kaisha,
1, Toyota-cho
Toyota-shi, Aichi-ken(JP)
Inventor: Katoh, Kenji
c/o Toyota Jidosha Kabushiki Kaisha,
1, Toyota-cho
Toyota-shi, Aichi-ken(JP)
Inventor: Kihara, Tetsuro
c/o Toyota Jidosha Kabushiki Kaisha,
1, Toyota-cho
Toyota-shi, Aichi-ken(JP)

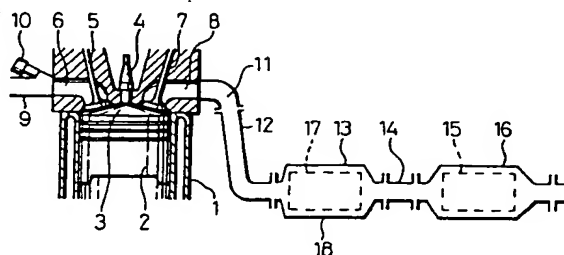
74 Representative: Tiedtke, Harro, Dipl.-Ing.
Patentanwaltsbüro
Tiedtke-Bühling-Kinne & Partner
Bavariaring 4
D-80336 München (DE)

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SEARCH REPORT

54 An exhaust gas purification device for an engine.

57 An engine comprising an exhaust passage having therein a NO_x absorbent which absorbs the NO_x when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is lean and releases the absorbed NO_x when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent becomes the stoichiometric air-fuel ratio or rich. A sulphur trapping device for trapping SO_x contained in the exhaust gas is arranged in the exhaust passage upstream of the NO_x absorbent.

Fig.1



BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an exhaust gas purification device for an engine.

2. Description of the Related Art

With respect to an engine in which a lean air-fuel mixture is burned, the same applicant has proposed a new type of engine in which a NO_x absorbent is arranged in the exhaust passage of the engine. This NO_x absorbent absorbs the NO_x when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is lean, and this NO_x absorbent releases the absorbed NO_x when the air-fuel ratio of exhaust gas flowing into the NO_x absorbent becomes rich. In this engine, the NO_x produced when the lean air-fuel mixture is burned is absorbed by the NO_x absorbent. The air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is temporarily made rich before the absorbing ability of the NO_x absorbent is saturated, and at this time, the NO_x is released from the NO_x absorbent. In addition, at this time, the NO_x thus released is reduced (See copending U.S. Patent Application No. 66,100 derived from PCT application FP92/01279).

However, since sulphur is contained in fuel and lubricating oil of the engine, sulphur oxides SO_x is contained in the exhaust gas and, in the above-mentioned engine, SO_x is absorbed in the NO_x absorbent together with NO_x . Nevertheless, even if the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is made rich, SO_x thus absorbed is not released from the NO_x absorbent, and thus the amount of SO_x stored in the NO_x absorbent is gradually increased. However, if the amount of SO_x stored in the NO_x absorbent is increased, the amount of NO_x which the NO_x absorbent is able to absorb is gradually reduced, and thus a problem arises in that NO_x cannot be absorbed in the NO_x absorbent.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an exhaust gas purification device capable of maintaining a high absorbing ability of the NO_x absorbent for a long time.

According to the present invention, there is provided an exhaust gas purification device of an engine having an exhaust passage, said device comprising: an NO_x absorbent arranged in the exhaust passage and absorbing NO_x when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is lean, said NO_x absorbent releasing ab-

sorbed NO_x when a concentration of oxygen in the exhaust gas flowing into the NO_x absorbent is lowered; and sulphur trapping means arranged in the exhaust passage upstream of the NO_x absorbent for trapping SO_x contained in the exhaust gas.

The present invention may be more fully understood from the description of a preferred embodiment of the invention set forth below, together with the accompanying drawings.

GRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

Fig. 1 is an overall view of an engine;

Fig. 2 is a diagram showing the concentration of unburned HC and CO and O_2 in the exhaust gas; and

Figs. 3A and 3B are views for explaining an absorbing and releasing operation of NO_x .

DESCRIPTION OF A PREFERRED EMBODIMENT

Referring to Figure 1, reference numeral 1 designates an engine body, 2 a piston, 3 a combustion chamber, and 4 a spark plug; 5 designates an intake valve, 6 an intake port, 7 an exhaust valve, and 8 an exhaust port. The intake port 6 is connected to the surge tank (not shown) via a corresponding branch pipe 9, and a fuel injector 10 injecting the fuel toward the interior of the intake port 6 is attached to each branch pipe 9. The exhaust port 8 is connected to a sulphur trapping device 13 via an exhaust manifold 11 and an exhaust pipe 12, and the sulphur trapping device 13 is connected to a casing 16 including a NO_x absorbent 18 via an exhaust pipe 14. In the engine illustrated in Fig. 1, the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 is normally made lean, and thus a lean air-fuel mixture is normally burned in the combustion chamber 3.

Figure 2 schematically shows the concentration of representative components in the exhaust gas discharged from the combustion chamber 3. As seen from Fig. 2, the concentration of the unburnt HC and CO in the exhaust gas discharged from the combustion chamber 3 is increased as the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 becomes richer, and the concentration of the oxygen O_2 in the exhaust gas discharged from the combustion chamber 3 is increased as the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 becomes leaner.

The NO_x absorbent 15 contained in the casing 16 uses, for example, alumina as a carrier. On this carrier, at least one substance selected from alkali metals, for example, potassium K, sodium Na, lithium Li, and cesium Cs; alkali earth metals, for example, barium Ba and calcium Ca; and rare earth

metals, for example, lanthanum La and yttrium Y and precious metals such as platinum Pt is carried. When referring to the ratio between the air and fuel (hydrocarbons) fed into the intake passage of the engine and the exhaust passage upstream of the NO_x absorbent 15 as the air-fuel ratio of the inflowing exhaust gas to the NO_x absorbent 15, this NO_x absorbent 15 performs the absorption and releasing operation of NO_x by absorbing the NO_x when the air-fuel ratio of the inflowing exhaust gas is lean, while releasing the absorbed NO_x when the concentration of oxygen in the inflowing exhaust gas falls. Note that, where the fuel (hydrocarbons) or air is not fed into the exhaust passage upstream of the NO_x absorbent 15, the air-fuel ratio of the inflowing exhaust gas coincides with the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3, and accordingly in this case, the NO_x absorbent 15 absorbs the NO_x when the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 is lean and releases the absorbed NO_x when the concentration of oxygen in the air-fuel mixture fed into the combustion chamber 3 is lowered.

When the above-mentioned NO_x absorbent 15 is disposed in the exhaust passage of the engine, this NO_x absorbent 15 actually performs the absorption and releasing operation of NO_x , but there are areas of the exact mechanism of this absorption and releasing operation which are not clear. However, it can be considered that this absorption and releasing operation is conducted by the mechanism as shown in Figs. 3A and 3B. This mechanism will be explained by using as an example a case where platinum Pt and barium Ba are carried on the carrier, but a similar mechanism is obtained even if another precious metal, alkali metal, alkali-earth metal, or rare-earth metal is used.

Namely, when the inflowing exhaust gas becomes very lean, the concentration of oxygen in the inflowing exhaust gas is greatly increased. At this time, as shown in Fig. 3A, the oxygen O_2 is deposited on the surface of the platinum Pt in the form of O_2^- . At this time, the NO in the inflowing exhaust gas reacts with the O_2^- on the surface of the platinum Pt and becomes NO_2 ($2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$). Subsequently, a part of the produced NO_2 is oxidized on the platinum Pt and absorbed into the absorbent. While bonding with the barium oxide BaO, it is diffused in the absorbent in the form of nitric acid ions NO_3^- as shown in Fig. 3A. In this way, NO_x is absorbed into the NO_x absorbent 15.

So long as the oxygen concentration in the inflowing exhaust gas is high, the NO_x is produced on the surface of the platinum Pt, and so long as the NO_x absorption ability of the absorbent is not saturated, the NO_x is absorbed into the absorbent and nitric acid ions NO_3^- are produced. Contrary

to this, when the oxygen concentration in the inflowing exhaust gas is lowered and the production of NO_2 is lowered, the reaction proceeds in an inverse direction ($\text{NO}_3^- \rightarrow \text{NO}_2$), and thus nitric acid ions NO_3^- in the absorbent are released in the form of NO_2 from the absorbent. Namely, when the oxygen concentration in the inflowing exhaust gas is lowered, the NO_x is released from the NO_x absorbent 15. As shown in Fig. 2, when the degree of leanness of the inflowing exhaust gas becomes low, the oxygen concentration in the inflowing exhaust gas is lowered, and accordingly when the degree of leanness of the inflowing exhaust gas is lowered, the NO_x is released from the NO_x absorbent 15 even if the air-fuel ratio of the inflowing exhaust gas is lean.

On the other hand, at this time, when the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 is made rich and the air-fuel ratio of the inflowing exhaust gas becomes rich, as shown in Fig. 2, a large amount of unburnt HC and CO is discharged from the engine, and these unburnt HC and CO react with the oxygen O_2^- on the platinum Pt and are oxidized. Also, when the air-fuel ratio of the inflowing exhaust gas becomes rich, the oxygen concentration in the inflowing exhaust gas is extremely lowered, and therefore the NO_2 is released from the absorbent. This NO_2 reacts with the unburnt HC and CO as shown in Fig. 3B and is reduced. In this way, when the NO_2 no longer exists on the surface of the platinum Pt, the NO_2 is successively released from the absorbent. Accordingly, when the air-fuel ratio of the inflowing exhaust gas is made rich, the NO_x is released from the NO_x absorbent 15 in a short time.

As mentioned above, when the air-fuel ratio of the inflowing exhaust gas is made lean, NO_x is absorbed in the NO_x absorbent 15 and, when the air-fuel ratio of the inflowing exhaust gas is made rich, NO_x is released from the NO_x absorbent 15 in a short time. Accordingly, in the engine illustrated in Fig. 1, when a time period during which a lean air-fuel mixture is burned exceeds a fixed time period, the air-fuel ratio of the air-fuel mixture fed into the engine cylinder is temporarily made rich to release NO_x from the NO_x absorbent 15.

However, SO_x is contained in the exhaust gas, and not only NO_x but also SO_x are absorbed in the NO_x absorbent 15. The mechanism of the absorption of SO_x into the NO_x absorbent 15 is considered to be almost the same as the absorption mechanism of NO_x . Next, this absorption mechanism of SO_x will be explained by using as an example a case where platinum Pt and barium Ba are carried on the carrier, as is the same manner as explaining the absorption mechanism of NO_x .

Namely, as mentioned above, when the air-fuel ratio of the inflowing exhaust gas is lean, the oxygen O_2 is deposited on the surface of the platinum Pt in the form of O_2^- . At this time, SO_2 in the inflowing exhaust gas reacts with the O_2^- on the surface of the platinum Pt and becomes SO_3 . Subsequently, a part of the produced SO_3 is oxidized on the platinum Pt and absorbed into the absorbent. While bonding with the barium oxide BaO, it is diffused in the absorbent in the form of nitric acid ions SO_4^{2-} , and sulfate $BaSO_4$ is produced.

However, this sulfate $BaSO_4$ is less easily dissociated and, even if the air-fuel ratio of the inflowing exhaust gas is made rich, this sulfate $BaSO_4$ remains as it stands without being dissociated. Accordingly, the amount of sulfate $BaSO_4$ increases as a time passes, and thus the amount of NO_x which the NO_x absorbent 15 is able to absorb is reduced as a time passes.

Therefore, in the present invention, to prevent SO_x from flowing into the NO_x absorbent 15, the sulphur trapping device 13 is arranged in the exhaust passage upstream of the NO_x absorbent 15. In this case, since the NO_x absorbent 15 absorbs SO_x , but does not release SO_x , an absorbent which is similar to the NO_x absorbent 15 can be used for the sulphur trapping device 13. In the embodiment illustrated in Fig. 1, the sulphur trapping device 13 comprises a SO_x absorbent 17 and a casing 18 surrounding the SO_x absorbent 17, and the SO_x absorbent 17 uses, for example, alumina as a carrier. On this carrier, at least one substance selected from alkali metals, for example, potassium K, sodium Na, lithium Li, and cesium Cs; alkali-earth metals, for example, barium Ba and calcium Ca; and rare-earth metals, for example, lanthanum La and yttrium Y and precious metals such as platinum Pt is carried.

In this case, with respect to the SO_x absorbent 17, it is not necessary to take a good absorbing and releasing operation of NO_x into consideration, but it is sufficient to take only a good trapping operation of SO_x into consideration, and therefore, it is preferable that the amount of the above-mentioned alkali metals, alkali earth metals or rare earth metals, contained in the SO_x absorbent 17 be increased as compared to the amount of those metals contained in the NO_x absorbent 15. In addition, cerium Ce may be added to the SO_x absorbent 17.

Where the SO_x absorbent 17 is arranged in the exhaust passage upstream of the NO_x absorbent 15 as illustrated in Fig. 1, the whole SO_x discharged from the engine is absorbed in the SO_x absorbent 17, and the SO_x absorbed in the SO_x absorbent 17 is not released even if the air-fuel ratio of air-fuel mixture fed into the combustion chamber 3 is made rich. Accordingly, only NO_x is absorbed in the NO_x absorbent 15, and thus it is

possible to prevent a NO_x absorbing ability of the NO_x absorbent 15 from being reduced.

Therefore, according to the present invention, it is possible to maintain a high NO_x absorbing ability of the NO_x absorbent 15 even if the NO_x absorbent 15 is used for a long time.

While the invention has been described by reference to a specific embodiment chosen for purposes of illustration, it should be apparent that numerous modifications could be made thereto by those skilled in the art without departing from the basic concept and scope of the invention.

An engine comprising an exhaust passage having therein a NO_x absorbent which absorbs the NO_x when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is lean and releases the absorbed NO_x when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent becomes the stoichiometric air-fuel ratio or rich. A sulphur trapping device for trapping SO_x contained in the exhaust gas is arranged in the exhaust passage upstream of the NO_x absorbent.

Claims

1. An exhaust gas purification device for an engine having an exhaust passage, said device comprising:
an NO_x absorbent arranged in the exhaust passage and absorbing NO_x when an air-fuel ratio of exhaust gas flowing into the NO_x absorbent is lean, said NO_x absorbent releasing an absorbed NO_x when a concentration of oxygen in the exhaust gas flowing into said NO_x absorbent is lowered; and
sulphur trapping means arranged in the exhaust passage upstream of said NO_x absorbent for trapping SO_x contained in the exhaust gas.
2. An exhaust gas purification device according to claim 1, wherein said sulphur trapping means comprises a SO_x absorbent which absorbs SO_x therein.
3. An exhaust gas purification device according to claim 2, wherein said SO_x absorbent contains at least one substance selected from alkali metals comprising potassium, sodium, lithium, cesium; alkali-earth metals comprising barium, calcium; and rare-earth metals comprising lanthanum, yttrium and contains platinum.
4. An exhaust gas purification device according to claim 3, wherein said NO_x absorbent contains at least one substance selected from alkali metals comprising potassium, sodium, lithium, cesium; alkali-earth metals comprising barium,

calcium; and rare-earth metals comprising lanthanum, yttrium and contains platinum, and an amount of said metals contained in said SO_x absorbent is larger than an amount of said metals contained in said NO_x absorbent.

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5. An exhaust gas purification device according to claim 1, further comprising air-fuel ratio control means for controlling said air-fuel ratio of exhaust gas to make said air-fuel ratio of exhaust gas lean when NO_x is to be absorbed in said NO_x absorbent and to make said air-fuel ratio of exhaust gas rich when NO_x is to be released from said NO_x absorbent.

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6. An exhaust gas purification device according to claim 5, wherein said air-fuel ratio control means controls said air-fuel ratio of exhaust gas by controlling an air-fuel ratio of air-fuel mixture fed into the engine.

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7. An exhaust gas purification device according to claim 1, wherein said NO_x absorbent contains at least one substance selected from alkali metals comprising potassium, sodium, lithium, cesium; alkali-earth metals comprising barium, calcium; and rare-earth metals comprising lanthanum, yttrium and contains platinum.

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Fig.1

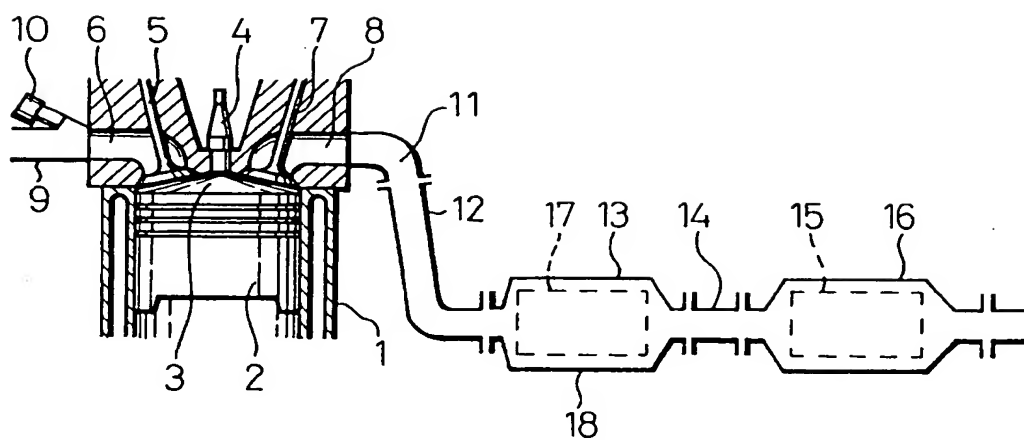


Fig.2

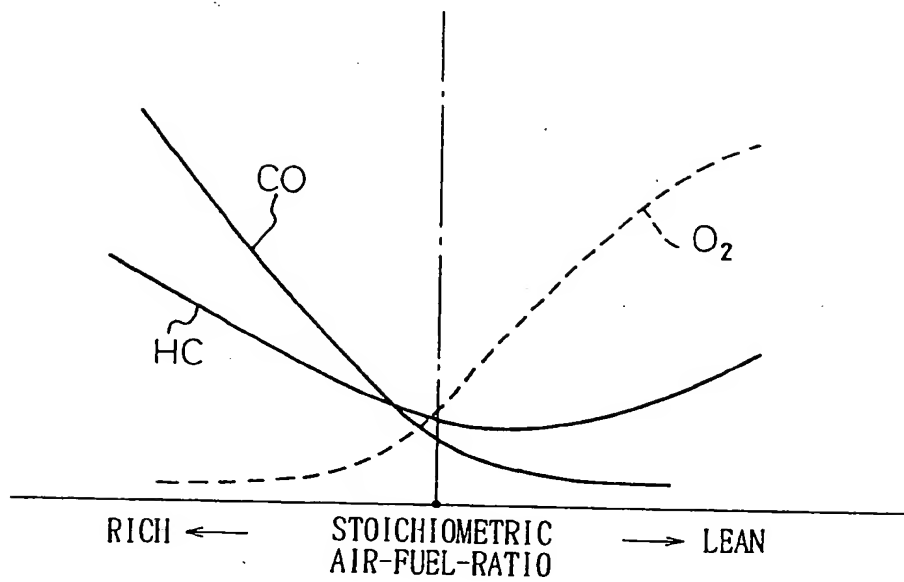


Fig.3A

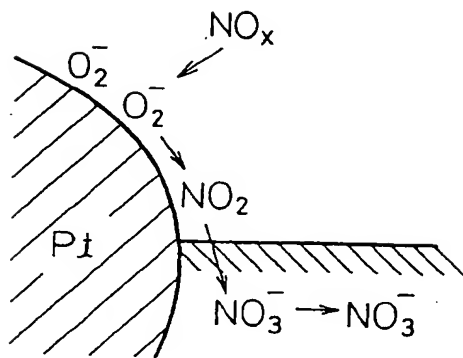
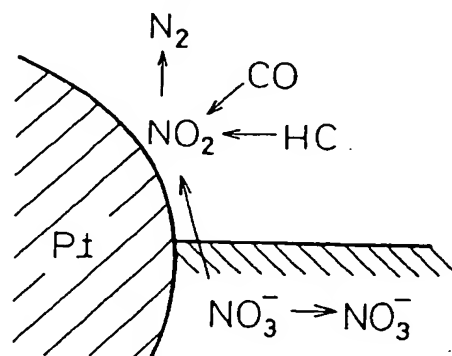


Fig.3B





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Application Number
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 November 1993	Examiner EIJKENBOOM, T
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EPO FORM 1500 03.92 (P04C01)



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